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Rare biscoumarins and a chlorogenic acid derivative from *Erycibe obtusifolia*

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Abstract

Three coumarins, 7,7′-dihydroxy-6,6′-dimethoxy-3,3′-biscoumarin (**1**), 7,7′-dihydroxy-6,6′-dimethoxy-8,8′-biscoumarin (**2**) and 7-O-[4′-O-(3″,4″-dihydroxycinnamyl)-β-D-glucopyranosyl]-6-methoxycoumarin (**3**), and a chlorogenic acid derivative, methyl-3-O-(4″-hydroxy-3″,5″-dimethoxybenzoyl)-chlorogenate (**4**) were isolated from the roots of *Erycibe obtusifolia* along with four known coumarins, scopoletin (**5**), scopolin (**6**), cleomiscosin A (**7**) and cleomiscosin B (**8**). Their structures were elucidated by spectroscopic methods. Among them, compounds (**1**) and (**2**) are rare carbon–carbon linked symmetrical biscoumarins.

Keywords: *Erycibe obtusifolia*; Convolvulaceae; Coumarin; Chlorogenic acid derivative; 7,7′-Dihydroxy-6,6′-dimethoxy-3,3′-biscoumarin; 7,7′-Dihydroxy-6,6′-dimethoxy-8,8′-biscoumarin

1. Introduction

Erycibe obtusifolia Benth (Convolvulaceae) is distributed in Southeast Asia and Australia. The roots, stems and twigs of the plant are also found in the south of China and are used in Chinese folk medicine to relieve symptoms of rheumatoid arthritis (Hsu et al., 1998). Up to now, less than 10 compounds, respectively as coumarins, alkaloids and chlorogenic acid, were reported from the plants of this genus (Yao and Chen, 1979; Wang et al., 1989; Song and Jin, 1997), of these, scopoletin and scopolin showed a strong anti-inflammatory activity and a tropanic alkaloid baogongteng A showed effects of a muscarinic agonist (Yao and Chen, 1979; Ye et al., 1981). In our further search for constituents from this plant, four new compounds which showed blue fluorescence under UV light (365 nm) including two biscoumarins (**1**), (**2**), a coumarin glucoside (**3**), and a chlorogenic acid derivative (**4**) were isolated from the roots of *Erycibe obtusifolia* along with four known coumarins, scopoletin (**5**), scopolin (**6**), cleomiscosin A (**7**) and cleomiscosin B (**8**). Their structures were established by spectroscopic methods. Biscoumarins **1** and **2** have rare symmetrical structures coupled through carbon–carbon bonds.

2. Results and discussion

Compound **1** was obtained as a yellow amorphous powder. Its molecular formula was determined to be $C_{20}H_{14}O_8$ from the HR–EI–MS ($[M]^+$, m/z found 382.0691, calcd 382.0689). The IR spectrum showed the presence of hydroxyl (3473 cm^{-1}), carbonyl (1718 cm^{-1}) groups, and aromatic rings (1612, 1576 and 1508 cm^{-1}). The ^1H NMR spectrum (Table 1) indicated the presence of three aromatic protons at δ 7.29 (1H, *s*), 6.83 (1H, *s*) and 8.30 (1H, *s*), a methoxy at δ3.83 (3H, *s*) and a hydroxy at δ 10.43 (1H, *s*). The ^{13}C NMR spectroscopic data (Table 1) showed 10 carbon signals, which were only half of the number of carbon atoms in the molecular formula of $C_{20}H_{14}O_8$. ^1H and

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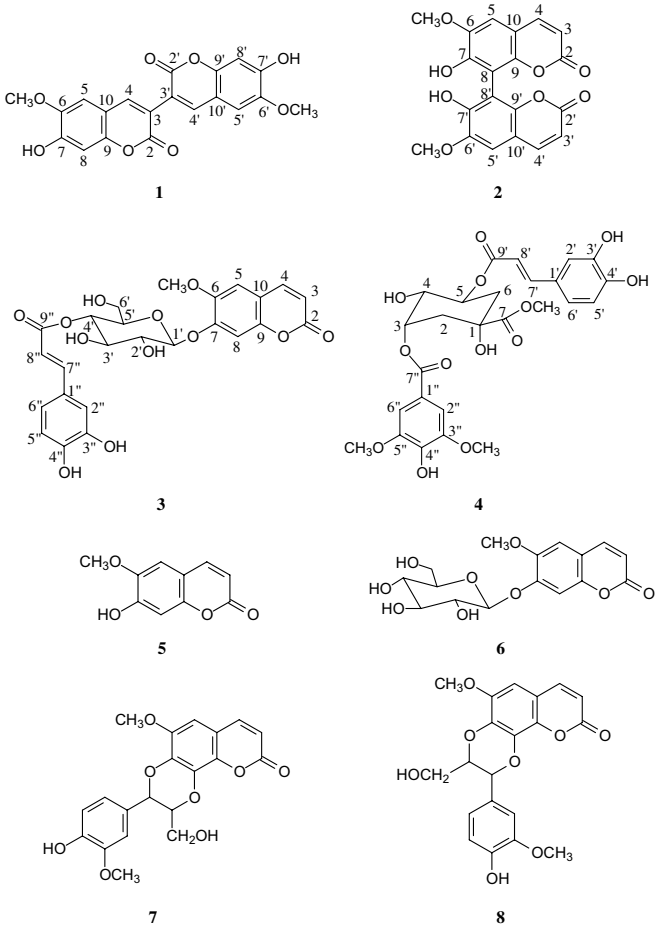
^{13}C NMR spectroscopic data of **1** were similar to the corresponding data of scopoletin (Abysher and Zmeikou, 1982; Kitajima et al., 2003). The differences were that H-3 signal had disappeared, while the chemical shifts of H-4 at δ 8.30 and C-3 at δ 117.0 were shifted downfield. These observations suggested that **1** was a symmetrical dimer of scopoletin at C-3. This was further confirmed by the HMBC spectrum (Fig. 1), which showed the vital correlations of H-4 at δ 8.30 with C-5 at δ 109.7 and C-3′ at δ 117.0. Thus, the structure of **1** was established as 7,7′-dihydroxy-6,6′-dimethoxy-3,3′-biscoumarin.



Compound **2** was obtained as a yellow amorphous powder. The IR spectrum showed the presence of hydroxyl (3327 cm^{-1}), carbonyl (1703 cm^{-1}) groups, and aromatic rings (1608, 1568 and 1495 cm^{-1}). The molecular formula of $C_{20}H_{14}O_8$ was determined by HR–EI–MS ([M]$^+$, *m/z* found 382.0716, calcd 382.0689). The ^{1}H NMR spectrum (Table 1) of **2** also showed three aromatic protons, but the difference from **1** was existence of an AX-system at δ 6.21 (1H, *d*, $J = 9.5$ Hz) and 7.99 (1H, *d*, $J = 9.5$ Hz). The ^{13}C NMR spectroscopic data (Table 1) showed 10 carbon signals, which were only half of the number of the carbon atoms in the molecular formula of $C_{20}H_{14}O_8$. These observations indicated that **2** was also a symmetrical dimer

Table 1
^{1}H NMR and ^{13}C NMR spectroscopic assignments for compounds **1** and **2** (DMSO-d_6)

C	**1**		**2**	
	δ_H(ppm), *J* (Hz)	δ_C	δ_H(ppm), *J* (Hz)	δ_C
2,2′		159.7		160.6
3,3′		117.0	6.21 *d* (9.5)	111.4
4,4′	8.30 *s*	143.0	7.99 *d* (9.5)	144.9
5,5′	7.29 *s*	109.7	7.34 *s*	108.7
6,6′		145.6		144.9
7,7′		151.6		149.4
8,8′	6.83 *s*	102.4		107.7
9,9′		149.0		147.8
10,10′		110.6		110.1
6,6′-OCH$_3$	3.83 *s*	56.1	3.90 *s*	56.1
7,7′-OH	10.43 *s*		9.81 *s*	

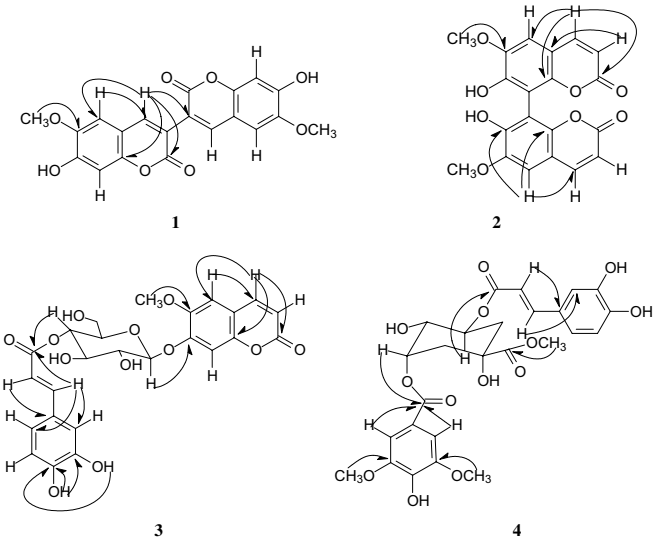


Fig. 1. Key HMBC correlations of compounds **1**–**4**.

of scopoletin coupled by a carbon–carbon bond. The linkage position was defined at C-8 based on the fact that the chemical shift of C-8 at δ 107.7 was shifted downfield, the H-8 signal had disappeared, and the long-range correlation of H-5 at δ 7.34 with C-4 at δ 144.9 was observed in the HMBC spectrum (Fig. 1). Thus, its structure was 7,7′-dihydroxy-6,6′-dimethoxy-8,8′-biscoumarin.

Compounds **1** and **2** are dimers of scopolin with carbon–carbon bonds. Because scopolin is present in 40–100 times of the amounts of our other metabolites in *E. obtusifolia*, compounds **1** and **2** might be formed as artifacts in our isolation process. In order to further confirm whether compounds **1** and **2** are either artifacts or new natural products, 100 mg of scopolin was dissolved either in 95% EtOH (20 ml) or in 95% EtOH (20 ml) and 10% acetic acid (0.5 ml) was heated for 10 h at reflux temperature. Compounds **1** and **2** were not formed as evidenced by HPLC analysis in both reactions. From the chemical synthetic perspective, the biscoumarins with carbon–carbon bond could be produced by the coupling of two coumarin mono-

Table 2
^{1}H NMR and ^{13}C NMR spectroscopic assignments for compounds **3** and **4** (DMSO-d_6)

C	**3**		C	**4**	
	δ_H(ppm), *J* (Hz)	δ_C		δ_H(ppm), *J* (Hz)	δ_C
2		160.4	1		72.7
3	6.33 *d* (10.0)	113.4	2	2.10, 2.04 *m*	35.5
4	7.96 *d* (10.0)	144.2	3	5.29 *m*	70.8
5	7.31 *s*	109.7	4	3.84 *m*	67.5
6		145.9	5	5.19 *m*	70.6
7		149.7	6	2.02, 2.24 *m*	34.7
8	7.19 *s*	103.0	7		173.9
9		148.8	7-OCH_3	3.60 *s*	51.9
10		112.4	1′		125.3
6-OCH_3	3.82 *s*	56.0	2′	7.03 *d* (1.5)	114.7
1′	5.23 *d* (7.0)	99.3	3′		145.6
2′	3.42 *m*	73.1	4′		148.5
3′	3.59 *m*	74.1	5′	6.77 *d* (7.5)	115.8
4′	4.75 *t*	70.7	6′	6.99 *dd* (7.5, 1.5)	121.3
5′	3.79 *m*	74.8	7′	7.42 *d* (15.5)	145.3
6′	3.42 *m*, 3.33 *m*	60.4	8′	6.15 *d* (15.5)	113.8
1″		125.5	9′		165.3
2″	7.05 *d* (1.5)	114.9	1″		120.0
3″		145.6	2″,6″	7.29 *s*	107.3
4″		148.4	3″,5″		147.4
5″	6.76 *d* (8.0)	115.8	4″		140.5
6″	7.02 *dd* (8.0, 1.5)	121.3	7″		165.1
7″	7.49 *d* (15.5)	145.5	3″,5″-OCH_3	3.81 *s*	56.1
8″	6.28 *d* (15.5)	113.9			
9″		165.8			

mers, in a process rationalized by means of free radical reactions. The conditions of the reactions are rigorous. The reactions can be brought about by oxidase enzymes, including peroxidase and laccase systems, known to be radical generators in plant (Dewick, 2002). But it is difficult that compounds **1** and **2** are formed under the conditions of our isolation process. Above all the information, compound **1** and **2** should be new natural products.

Compound **3** was obtained as a white amorphous powder. The IR spectrum showed the presence of hydroxyl (3219 cm^{-1}), carbonyl (1722 cm^{-1}) groups, and aromatic rings (1608, 1570 and 1514 cm^{-1}). Its molecular formula was determined to be $C_{25}H_{24}O_{12}$ from the HR-ESI-MS ($[M+Na]^+$, *m/z* found 539.1169, calcd 539.1165). In the ^{1}H NMR spectrum (Table 2), two sets of AX-type signals were observed. Due to the vicinal coupling constants, the signals at δ 6.33 (1H, *d*, $J = 10.0$ Hz) and 7.96 (1H, *d*, $J = 10.0$ Hz) were assigned to a *cis* configured double bond, whereas the signals at δ 6.28 (1H, *d*, $J = 15.5$ Hz) and δ 7.49 (1H, *d*, $J = 15.5$ Hz) were assigned to a *trans* configured double bond. An ABX-system at δ 7.05 (1H, *d*, $J = 1.5$ Hz), 7.02 (1H, *dd*, $J = 8.0$, 1.5 Hz) and 6.76 (1H, *d*, $J = 8.0$ Hz) indicated the presence of a 1,3,4-trisubstituted benzene ring in **3**. Additionally, the ^{1}H NMR spectrum showed two aromatic protons at δ 7.31 (1H, *s*) and 7.19 (1H, *s*), a methoxy at δ 3.82 (3H, *s*), and an anomeric proton signal at δ 5.23 (1H, *d*, $J = 7.0$ Hz). The^{13}C NMR spectrum of **3** showed 25 carbon signals (Table 2). Except for 10 carbon signals assigned as a scopoletin moiety and six saccharide carbon signals, the remaining nine carbon signals were similar to the corresponding carbon of a caffeoyl unit (De Rosa et al., 2002). The above analysis suggested that **3** was a scopoletin caffeoylglycoside. The carbon signals at δ 99.3, 73.1, 74.1, 70.7, 74.8, and 60.4 in the ^{13}C NMR and an anomeric proton signal at δ 5.23 (1H, *d*, $J = 7.0$ Hz) in the ^{1}H NMR spectrum indicated that the sugar was β-D-glucose (Tsukamoto et al., 1985). The acylated location was determined at C-4′ of the glucose based on the facts of acylation shifts principle and HMBC spectrum which showed the correlations between H-4′ at δ 4.75 and C-9″ at δ 165.8, C-6′ at δ 60.4 (Fig. 1). On the other hand, the correlation of H-1′ at δ 5.23 with C-7 at δ 149.7 was observed in the HMBC spectrum (Fig. 1). From the above evidence, the structure of **3** was established as 7-O-[4′-O-(3″,4″-dihydroxycinnamyl)-β-D-glucopyranosyl]-6-methoxycoumarin.

Compound **4** was obtained as a white amorphous powder. The IR spectrum showed the presence of hydroxyl (3408 cm^{-1}), carbonyl (1697 cm^{-1}) groups, and aromatic rings (1606 and 1516 cm^{-1}). Its molecular formula was determined to be $C_{26}H_{28}O_{13}$ from the HR–ESI–MS ($[M+Na]^+$, *m/z* found 571.1415, calcd 571.1427). In the ^{1}H NMR spectrum (Table 2), an ABX-system at δ 7.03 (1H, *d*, $J = 1.5$ Hz), 6.99 (1H, *dd*, $J = 7.5$, 1.5 Hz) and 6.77 (1H, *d*, $J = 7.5$ Hz) indicated the presence of a 1,3,4-trisubstituted benzene, and an AX-system at δ 7.42 (1H, *d*, $J = 15.5$ Hz) and 6.15 (1H, *d*, $J = 15.5$ Hz) suggested the *trans*-configuration for a double bond. Additionally,

the ^{1}H NMR spectrum showed two aromatic protons at δ 7.29 (2H, *s*), three methoxy groups at δ 3.81 (6H, *s*) and 3.60 (3H, *s*), three oxygenated methine protons at δ 5.29 (1H, *m*, H-3), 5.19 (1H, *m*, H-5), 3.84 (1H, *m*, H-4), and four methylene protons at δ 2.04, 2.10 (2H, *m*, H-2) and 2.02, 2.24 (2H, *m*, H-6). The ^{13}C NMR spectrum (Table 2) of **4** showed 26 carbon signals, seventeen of which were similar to a methyl chlorogenate moiety (Deyama et al., 1987). The extra nine carbon signals were assigned as a 4″-hydroxy-3″,5″-dimethoxybenzoyl moiety according to the ^{1}H NMR spectroscopic data. Compared with the corresponding NMR data of methyl chlorogenate (Deyama et al., 1987), the signals of C-2 at δ 35.5, C-4 at δ 67.5 in **4** were shifted significantly upfield and the signal of C-3 at δ 70.8 in **4** was shifted downfield, indicating that 4″-hydroxy-3″,5″-dimethoxybenzoyl was at C-3 in **4**. This was confirmed by the NOE and the HMBC spectra (Fig. 1). In a NOE experiment, an obvious enhancement of H-3 at δ 5.29 was observed upon irradiation of H-4 at δ 3.84, while in the HMBC spectrum (Fig. 1) the key correlations between H-3 at δ 5.29 and C-7″ at δ 165.1 was exhibited. Thus, structure of **4** was established as methyl-3-O-(4″-hydroxy-3″,5″-dimethoxybenzoyl)-chlorogenate.

In addition, the four known compounds were identified by spectroscopic methods as scopoletin (**5**) (Abysher and Zmeikou, 1982), scopolin (**6**) (Tsukamoto et al., 1985), cleomiscosin A (**7**) (Ray et al., 1985) and cleomiscosin B (**8**) (Ray et al., 1985).

3. Concluding remarks

The genus of *Erycibe* belongs to Convolvulaceae and comprises about 66 species, which are mainly found in Asia. Four of them, *E. obtusifolia*, *E. schmidtii*, *E. hainanesis* and *E. elliptilimba*, were chemically investigated. Coumarins and alkaloids were considered as the characteristic constituents in the genus of *Erycibe* (Yao and Chen, 1979; Wang et al., 1989; Song and Jin, 1997; Lu et al., 1986). In our further search for constituents, seven coumarins were isolated from the roots of *Erycibe obtusifolia*. Among them **1** and **2** were symmetrical biscoumarins. To our knowledge this was the first report on the biscoumarin in the family of Convolvulaceae. Similar coumarin patterns with carbon–carbon bonds were previously obtained from *Impatiens balsamina* L. (Panichayupakaranant et al., 1998) *Daphne oleoides* (Ullah et al., 1999; Riaz and Malik, 2001), *Toddalia asiatica* (L.) Lam. (Tsai et al., 1997), *Gnidia socotrana* (Balf. f.) Gilg (Franke et al., 2002), *Daphne giraldii* Nitsche (Li et al., 2005), *Ipomopsis aggregata* (Pursh) V. Grant (Arisawa et al., 1984), *Lasiosiphon eriocephalus* Decne (Sengupta and Das, 1978), *Boenninghausenia albiflora* Reichb & Meissner (Joshi et al., 1989), *Edgeworthia chrysantha* Lindl. (Baba et al., 1990) the mycelium of *Emericella desertorum* Samson & Mouchacca, strain CBS 653.73 (Nozawa et al., 1987), the fungal metabolite of *Aspergillus niger* (ATCC accession no. 36626) (Cutler et al., 1979). Among them, five were symmetrical structures. From a biosynthetic pathway perspective, the biscoumarins with carbon–carbon bonds could be formed by oxidative coupling (Dewick, 2002). Our findings of two biscoumarins could be regarded as some further insight into the diversity of natural products in the genus *Erycibe*.

4. Experimental

4.1. General

All melting points were determined on a Reichert Nr-229 micromelting point apparatus and are uncorrected. The optical rotations were measured on a Perkin–Elmer 341LC polarimeter. UV spectra were recorded on HP 8453 UV–Visible spectrophotometer. IR spectra were recorded on an IMPACT 400 (KBr) spectrometer. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), NOE and HMBC spectra were run on an INOVA-500 spectrometer with tetramethylsilane (TMS) as internal standard and values were given in ppm (δ). Electrospray ionization (ESI) was performed on Agilent 1100 series LC/MSD Trap mass spectrometer (SL). EI–MS and HR–EI–MS was performed on AutoSpec Ultima-TOF mass spectrometer. HR–ESI–MS was performed on Finnigan LTQ FTMS. Silica gel (100–200, 200–300 mesh) (Qingdao) Sephadex LH-20 (Pharmacia Fine Chemicals), and ODS (YMC) was used for column chromatography (CC) and silica gel GF-254 (Qingdao) for TLC.

4.2. Plant material

The roots of *Erycibe obtusifolia* Benth were collected in July 2005 in Hainan Province of People's Republic of China. The plant material was identified by Professor Shi-Man Huang. A voucher specimen (21180) was deposited in the Herbarium of the Department of Medicinal plants, Institute of Materia Media, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, PR China.

4.3. Extraction and isolation

The dried roots of *Erycibe obtusifolia* Benth (8.9 kg) were exhaustively extracted three times with 95% EtOH (50 L) for 2 hours at reflux temperature. Then the EtOH extract was concentrated under reduced pressure to give a residue (450 g), which was suspended in H_2O, extracted successively with petroleum ether, EtOAc and *n*-BuOH. The combined EtOAc parts were evaporated to dryness in *vacuo* to give a residue (190 g), with the latter was subjected to CC silica gel using petroleum ether/acetone (in gradient) as the eluting solvent, followed by MeOH to yield 18 fractions. **5** (1000 mg) was crystallized from fraction7 [petroleum ether/acetone (25:1)] as yellow crystals. **1** (25 mg) was crystallized from fraction 10 [petroleum

ether/acetone (10:3)] as a yellow amorphous powder. **7** (15 mg) was crystallized from fraction 11 [petroleum ether/acetone (3:1)] as a yellow amorphous powder. Fraction 12 [petroleum ether/acetone (2:1), 3 g] was applied to a silica gel column using a $CHCl_3$/MeOH (gradient) as eluting solvent to yield 8 subfractions, and **8** (12 mg) was crystallized from subfraction 2 as a yellow amorphous powder. Fraction 14 [petroleum ether/acetone (4:3), 6 g] was subjected to silica gel CC using a $CHCl_3$/MeOH (gradient) as eluting solvent to yield 10 subfractions, and **2** (10 mg) was crystallized from subfraction 2 as a yellow amorphous powder. Fraction 15 [petroleum ether/acetone (1:1), 22 g] was applied again to silica gel using a $CHCl_3$/MeOH (gradient) as eluting solvent to yield 12 subfractions. Subfraction 4 (1 g) was applied to ODS using MeOH:H_2O (gradient) to yield 8 parts, and part 3 was then applied to Sephadex LH-20 using MeOH and gave compound **4** (20 mg). Fraction 17 (acetone, 9 g) was subjected to silica gel CC using a $CHCl_3$-MeOH (gradient) as eluting solvent to yield 10 subfractions, and **3** (25 mg) was crystallized from subfraction 6 as a white amorphous powder. **6** (400 mg) was crystallized from fraction18 (MeOH) as white crystals.

4.4. Characterization

4.4.1. 7,7′-Dihydroxy-6,6′-dimethoxy-3,3′-biscoumarin (*1*)

Yellow amorphous powder, m.p. 253–255 °C. $[\alpha]_D^{25}$ 0°(CH_3OH; c 0.05). UV (CH_3OH) λ_{max} nm (logε): 331 (4.08), 287 (3.86); IR (KBr) ν_{max} cm^{-1}: 3473, 3059, 2918, 2850,1718, 1612, 1576, 1508, 1308, 1273, 1217, 1167, 1005, 949, 866, 766, 596; For ^1H (DMSO-d_6, 500 MHz) and ^{13}C (DMSO-d_6, 125 MHz) NMR spectra, see Table 1; EI-MS *m*/*z* (rel. int.): 382 $[M]^+$ (100), 354 (6), 339 (23), 181 (9); HR-EI-MS *m*/*z*: 382.0691$[M]^+$ (calcd for $C_{20}H_{14}O_8$, 382.0689).

4.4.2. 7,7′-Dihydroxy-6,6′-dimethoxy-8,8′-biscoumarin (*2*)

Yellow amorphous powder, m.p. 233–235 °C. $[\alpha]_D^{25}$ 0°(CH_3OH; c 0.04). UV (CH_3OH) λ_{max} nm (logε): 347 (4.04), 264 (3.90); IR (KBr) ν_{max} cm^{-1}: 3327, 3062, 2918, 2850, 1703, 1608, 1568, 1469, 1417, 1288, 1265, 1209, 1161, 1034, 955, 860, 758, 596; For ^1H (DMSO-d_6, 500 MHz) and ^{13}C (DMSO-d_6, 125 MHz) NMR spectra, see Table 1; EI-MS *m*/*z* (rel. int.): 382 $[M]^+$ (8), 230 (16), 117 (91), 115 (100); HR-EI-MS *m*/*z*: 382.0716 $[M]^+$ (calcd for $C_{20}H_{14}O_8$, 382.0689).

4.4.3. 7-O-[4′-O-(3″,4″-Dihydroxycinnamyl)-β-D-glucopyranosyl]-6-methoxycoumarin (*3*)

White amorphous powder, m.p. 245–247 °C. $[\alpha]_D^{25}$ −32°(CH_3OH; c 0.05). UV (CH_3OH) λ_{max} nm (logε): 333 (4.25), 292 (4.09). IR (KBr) ν_{max} cm^{-1}: 3219, 2918, 2850, 1722, 1608, 1570, 1514, 1448, 1388, 1284, 1153, 1082, 924, 885, 818, 758, 588; For ^1H (DMSO-d_6, 500 MHz) and ^{13}C (DMSO-d_6, 125 MHz) NMR spectra, see Table 2; ESI-MS *m*/*z* (rel. int.): 539 $[M+Na]^+$ (100), 517 (44), 301 (28), 245 (28); HR-ESI-MS *m*/*z*: 539.1169 $[M+Na]^+$ (calcd for $C_{25}H_{24}O_{12}Na$, 539.1165).

4.4.4. Methyl-3-O-(4″-hydroxy-3″,5″-dimethoxybenzoyl)-chlorogenate (*4*)

White amorphous powder, m.p. 139–141 °C. $[\alpha]_D^{25}$ −78°(CH_3OH; c 0.05). UV (CH_3OH) λ_{max} nm (logε): 330 (4.26), 287 (4.34); IR (KBr) ν_{max}: 3408, 2951, 2844, 1697, 1606, 1516, 1460, 1334, 1275, 1232, 1184, 1113, 1032, 984, 957, 858, 814, 764, 604 cm^{-1}; For ^1H (DMSO-d_6, 500 MHz) and ^{13}C (DMSO-d_6, 125 MHz) NMR spectra, see Table 2; ESI-MS *m*/*z* (rel. int.) 571 $[M+Na]^+$ (100), 505 (42), 284 (42); HR-ESI-MS *m*/*z*: 571.1415 $[M+Na]^+$ (calcd for $C_{26}H_{28}O_{13}Na$, 571.1427).

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